



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : G03C 5/00	A1	(11) International Publication Number: WO 87/ 03387 (43) International Publication Date: 4 June 1987 (04.06.87)
<p>(21) International Application Number: PCT/US86/02441</p> <p>(22) International Filing Date: 12 November 1986 (12.11.86)</p> <p>(31) Priority Application Numbers: 802,514 823,942 879,385</p> <p>(32) Priority Dates: 27 November 1985 (27.11.85) 29 January 1986 (29.01.86) 27 June 1986 (27.06.86)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: MACDERMID, INCORPORATED [US/ US]; 50 Brookside Road, Waterbury, CT 06708 (US).</p> <p>(72) Inventors: GRUNWALD, John, J. ; 161 Whittier Road, New Haven, CT 06515 (US). SPENCER, Allen, C. ; 45 Longwood Drive, Naugatuck, CT 06770 (US).</p>		<p>(74) Agent: ST. ONGE, Ronald, J.; St. Onge, Steward, Johnston & Reens, 986 Bedford Street, Stamford, CT 06905 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), CH (European patent), DE (Euro- pean patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European pa- tent), NL (European patent), SE (European patent).</p> <p>Published With international search report. With amended claims.</p>
(54) Title: THERMALLY STABILIZED PHOTORESIST IMAGES		
(57) Abstract Photoresist image layers, particularly those used for high resolution geometries in microelectronic applications, are stabilized against distortion or degradation by the heat generated during subsequent etching, ion implantation processes and the like, by the application of a film of a thermally stabilizing agent prior to postdevelopment bake of the image layer. The process serves to achieve thermal stabilization of the photoresist image layer without significantly affecting the ease of subsequent stripping of the layer. It is particularly effective when used to thermally stabilize positive resist images derived from photoresist systems based on novolak resins.		

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THERMALLY STABILIZED PHOTORESIST IMAGESBackground of the Invention1. Field of the Invention

5 This invention relates to an improved process for thermally stabilizing photoresist images and is more particularly concerned with the thermal stabilization of photoresist images having high resolution geometries for use in microelectronic applications.

2. Description of the Prior Art

10 As technology in the semi-conductor industry advances there is an increasing need for photoresist systems which can provide high resolution images having lines which are often below 1 micron in width. Positive resist systems are gaining popularity for producing such
15 images. Typical of such systems are those based on novolak resins, used in a solvent base with a photosensitizer such as an ester of 1-oxo-2-diazo-naphthoquinone-5-sulfonic acid. The photoresist system of this type is coated on an appropriate substrate such as a
20 silicon wafer whose surface has been treated to form oxides, metals, nitrides, phosphides and the like. The coated substrate is covered with a mask, exposed through the mask using appropriate UV radiation (often monochromatic) and then developed using an alkaline developer.
25 The image present on the mask is thereby reproduced on

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the substrate, the areas of the photoresist layer, which were exposed to radiation by passage through the transparent portions of the mask, having been rendered soluble in the alkaline developer and therefore having been removed during the developing step. The unexposed portions of the photoresist layer, corresponding to the opaque portions of the mask, remain on the substrate. The developed image layer and substrate is then exposed to a post-development bake, to cure the photoresist remaining on the substrate and enhance the adhesion thereof to the substrate, before subjecting the image and substrate to the pattern generation step. The thermal curing of the photoresist may also take place if the photoresist and substrate are subjected to a later step involving exposure to heat and, in such circumstances, a specific post-development bake may not be required. The pattern generation step comprises etching, ion implantation doping, metal deposition and the like to produce the final desired image (e.g. an integrated circuit) on the substrate. Thereafter, in a final step, the remaining photoresist is stripped from the substrate using appropriate solvents or other techniques known in the art.

A number of problems arise when applying such techniques to the production of high resolution images. The harsh environment, usually including elevated temperatures, created in the etching, ion implantation and like techniques employed in the pattern generation step of the process frequently causes the photoresist image to lose its integrity either by softening and flowing, edge rounding, charring, cracking and the like. This loss of integrity is reflected in loss of the desired features in the final product of the process. Further, in order to prevent attack on the photoresist leading to failure of the latter and thus attack on the underlying substrate in places which the photoresist was designed to

protect, it is frequently the practice to employ thicknesses of photoresist layer which are high in relation to the line widths in the image. Ratios of photoresist thickness to line widths as high as 2:1 have been employed. This is commonly referred to in the art as the use of a high aspect ratio image. As will be apparent to one skilled in the art, the use of such high aspect ratios is often difficult to achieve especially when geometries shrink below 1 micron.

It is accordingly desirable to be able to produce high resolution photoresist images which are also capable of surviving exposure to the high temperatures involved in the post-imaging processes without losing their integrity. A number of attempts to achieve such photoresist images have been reported. Illustratively, Ma U.S. Patent 4,187,331 teaches the heat stabilization of a resist image layer by subjecting the latter to an electrodeless flow discharge under low pressure in an atmosphere containing an organic fluorine compound such as carbon tetrafluoride.

Verelst et al. U.S. Patent 3,652,274 describes the preparation of a metal printing plate in which a photoresist image is produced on the metal substrate and the image is developed using a hydrophobizing agent in the development fluid in order to increase the resistance of the image to the etching fluid used in the subsequent step. The hydrophobizing agent can be a fluoroalkyl-substituted organic silane.

Tada et al. U.S. Patent 4,454,222 teaches the preparation of high resolution photoresist images using as the photoresist resin a polymer derived from trifluoroethyl-2-chloroacrylate and employing certain ketones as developers for the exposed image.

Matthews U.S. Patent 4,548,688 describes hardening the photoresist by exposure to UV radiation. This method can cause difficulty in subsequent stripping of

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the photoresist, as well as introducing an additional equipment handling step in the overall process of producing the final product.

5 Chin et al. U.S. Patent 4,125,650 describes hardening photoresist images by chemically bonding a layer of a quinone-diazide hardening agent to the image. Cratering of the unexposed photoresist in positive photoresist images is said to occur due to gas evolved by the diazo compound during the baking step of the process. The
10 coated image is also rendered more difficult to remove from the substrate after pattern generation has been completed.

It has now been found that high resolution photoresist images which are stabilized against distortion
15 and other forms of thermal degradation during post-imaging treatments of the imaged substrate, can be produced by a novel process which will be described hereinafter.

SUMMARY OF THE INVENTION

It is an object of the invention to provide high
20 resolution photoresist images which will withstand exposure to elevated temperatures up to about 220°C. during post-imaging processes without suffering significant distortion or other deterioration of the image profile.

25 It is a further object of the invention to provide a simple, relatively inexpensive, process for treating a high resolution photoresist image after development and preferably prior to post-development bake whereby the image is stabilized against distortion or other forms of
30 degradation in subsequent post-imaging processes.

It is yet another object of the invention to provide a process for thermally stabilizing a high resolution photoresist image on a substrate without significantly affecting the ease of subsequently stripping said photoresist from the substrate.
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Another object of the invention is to dye the photoresist after exposure and development to make it visible for inspection purposes. The resist layer is so thin, typically less than 2 microns, that its inherent color is attenuated below visible recognition.

These objects, and other objects which will become apparent from the description which follows, are achieved by the process of the invention which, in its broadest aspect, comprises a process for thermally stabilizing a photoresist image layer formed on a substrate wherein the image layer, prior to being subjected to a post-development bake, is coated with a protective film of a material which, as discussed in detail below, bonds to the photoresist but is substantially rinsed from the exposed substrate after post bake and which does not interfere with the desired operation of any of the subsequent steps of pattern generation including final removal of the photoresist image. Optionally the protective film also contains a dyestuff.

The process of the invention can be utilized to thermally stabilize any type of photoresist image supported by a substrate. It is particularly advantageous when utilized to treat high resolution positive photoresist images supported on substrates such as silicon, silicon oxide, metals, nitrides, phosphides and the like. In a particularly preferred embodiment of the process of the invention the latter is employed to thermally stabilize a high resolution positive photoresist image which has been prepared using a photoresist system based on a novolak resin.

The invention also comprises high resolution photoresist images supported on substrates, which images have been stabilized against distortion and other degradation which would otherwise be caused by the image during post-development processing of the substrate.

DETAILED DESCRIPTION OF THE INVENTION

As set forth above, the process of the invention can be employed to thermally stabilize any photoresist image formed on a substrate. The formation of the image on the substrate can be carried out by any of the procedures well known and conventionally used in the art. Similarly, the steps to which the image and supporting substrate are subjected, before and after the process of the invention has been carried out on the image, can be any of those well-known and practiced in the art. Illustrative of the steps involved in the preparation of a high (often sub-micron) resolution positive resist image, and its processing by plasma etching to produce geometries which can be sub-micron on silicon wafers and like substrates, are those described by Grunwald et al. in a paper presented at the SPIE Conference on Microlithography, Santa Clara, California, March 1984.

The process of the invention is interposed as a novel step in these known and conventionally used processes after the photoresist image has been developed on the substrate but preferably prior to the post-development baking step or prior to exposure to heat generated in the subsequent pattern generation step as discussed above. The novel process step of the invention comprises applying a coating of a protective film of thermally stabilizing material to the surface of the photoresist image.

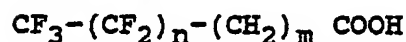
The thermally stabilizing material can be any of a wide variety of high temperature resistant materials which meet certain parameters. Thus the material is capable of being applied in solution or as a dispersion in an appropriate medium (preferably water) to form a thin film by coating using spin coating and the like techniques conventionally employed in the art. Secondly, the material bonds sufficiently to the surface of

the photoresist image during the heating process so that, after post-baking, excess material can be rinsed using appropriate solvents (preferably water) from other portions of the coated substrate without removing any significant amount of the material on the photoresist image. Thirdly, the material is such that it does not interfere with any of the subsequent steps, i.e. the steps of pattern generation and photoresist removal to which the treated image is to be subjected. Finally the material when applied as a coating to the photoresist image serves to stabilize the latter to exposure to temperatures of at least about 140°C and preferably to temperatures at least as high as about 175°C. Illustrative of materials which meet the above criteria and which can be employed in the process of the invention are fluorocarbon surfactants, film forming polymers, chromium sulfate, trichloroacetic acid, chromotropic acid (4,5-dihydroxy-2,7-naphthalene-disulfonic acid) and salts thereof such as the di-alkali metal salts, and the like. Other materials which meet the above parameters will be apparent to one skilled in the art.

The perfluorocarbon surfactants which are employed as one of the thermally stabilizing materials in the novel process of the invention are a class of compounds well-known and recognized in the art. Thus, this class of compounds is characterized by the presence of a perfluoroalkyl group $\text{CF}_3-(\text{CF}_2)_n$ united directly or through a polymethylene group $-(\text{CH}_2)_m$ to a hydrophilic group such as a carboxylic, sulfonic or phosphonic acid group, either in the form of the free acid or a salt or ester thereof, a polyether moiety such as $\text{R}-(\text{CH}_2\text{CH}_2\text{O})_x$ wherein R is hydrogen or methyl, x has a value of about 8 to about 20, and quaternary ammonium groups.

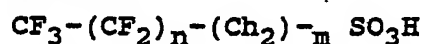
Illustrative of perfluorocarbon surfactants are:

- (i) perfluorocarbon-carboxylic acids of the general formula



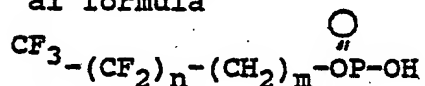
wherein n has a value of about 6 to about 16 and m has a value of 0 to about 8, and the alkali metal, ammonium and tertiary amine salts of the above acids;

- (ii) perfluorocarbon-sulfonic acids of the general formula



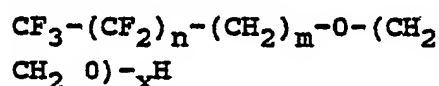
wherein n and m have the values set forth above, and the alkali metal, ammonium and tertiary amine salts of the above acids;

- (iii) perfluorocarbon-phosphonic acids of the general formula



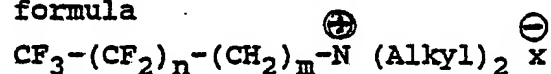
wherein n and m have the values set forth above, and the alkali metal, ammonium and tertiary amine salts of the above acids;

- (iv) O-perfluoroalkyl polyethylene glycols of the general formula



wherein n, m and x have the values set forth above; and

- (v) quaternary ammonium salts of N-perfluoroalkyl-N', N"-dialkylamine of the general formula



wherein x is a cation derived from an organic acid such as acetic, propionic and the like or inorganic acid such as hydrochloric, hydriodic,

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hydrobromic and the like, and n and m have the values set forth above;

5 Mixtures of two or more different perfluorocarbon surfactants can be employed if desired provided that the combined amount of the surfactants in the mixture, which is employed in the coating solution used in the process of the invention, lies within the ranges set forth above.

10 While all the above types of perfluorocarbon surfactant have some solubility in water or in a mixture of water and a lower aliphatic alcohol such as methanol, ethanol, isopropyl alcohol, and the like, the solubility can be enhanced, if desired or if necessary, by employing a non-fluorine-containing surfactant in combination
15 with the perfluorocarbon surfactant. Any of the surfactants, anionic, cationic or non-ionic, known in the art can be employed for this purpose.

20 Illustrative of the perfluorocarbon surfactants which can be employed in the process of the inventions are those which are available from E. I. duPont under the trademark ZONYL and those available from 3M Company under the trademark FLUORAD.

25 Illustrative of film forming polymers which are employed as thermally stabilizing agents in the process of the invention are carboxymethyl cellulose, carboxyethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyalkylene oxides such as polyethylene oxide, polypropylene oxide and the like, hydrolyzed collagen, and other gelatinous colloidal materials such as pectin,
30 gum tragacanth, gum arabic and the like. The term "hydrolyzed collagen" is inclusive of gelatin and glue derived from sources of collagen such as animal tissue, bones, sinews, hides and the like by hydrolysis (acid or alkaline) or by enzymolysis, as well as further hydro-
35 lyzed versions of gelatin and glue. Gelatin and glue

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are very similar chemically but gelatin is the name given to the prot inaceous product obtained in a purity suitable for edible consumption while glue is the name given to the product obtained in a purity suitable only for non-food uses.

A preferred film forming polymer for use in the present invention is gelatin. Any of the various grades of gelatin including Type A (acid) and Type B (alkali) can be employed. Advantageously the bloom is typically within the range of about 100 to about 275 but the particular bloom is not critical. Indeed, especially preferred film formers for use in the process of this invention are non-gelling hydrolysates of gelatin, such as those obtained from acid or alkaline hydrolysis of Type A or Type B gelatins, particularly those having molecular weights in the 1000 to 5000 range.

Advantageously the thermally stabilizing material is employed as a solution in water or in water-miscible solvents such as ethanol, isopropanol, and the like lower aliphatic alcohols, and is applied by any appropriate coating technique such as dip-coating, roller coating, spray-coating, spin-coating and the like. Spin-coating is a particularly preferred technique in the processing of wafers.

The application of the solution of the above material is carried out advantageously at ambient temperature but elevated temperatures, i.e. temperatures up to about 120°C, can be employed if desired, provided such temperatures have no adverse effect on the photoresist. The concentration of the thermally stabilizing material employed in the coating solution can vary over a wide range from about 0.1 about 10 percent by weight. Preferably the material is employed in a concentration of about 0.5 to about 5 percent by weight and, most preferably, in a range of about 1 to about 2 percent by weight.

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The amount of thermally stabilizing material which is applied to the surface of the photoresist image in the above manner is not critical provided that the added film thickness is not so large as to alter significantly the geometry and profile of the image being coated. The spin-coating method of application is particularly advantageous because it leaves only a thin film on the image and any excess is spun-off.

After the coating has been applied in the above manner, the coated image and supporting substrate is then subjected to the post-development bake normally employed in the conventional processes of the art discussed above. This bake step is advantageously carried out at a temperature in the range of about 100°C to about 190°C or higher provided that the particular temperature chosen in any given instance is such that no significant change of profile or critical dimensions (CDs) of the photoresist image is produced during the baking step. The time for which the baking is continued is not critical and is generally of the order of about 10 minutes to about 30 minutes. The time of baking employed in any given instance is dependent on the bake temperature employed and on the nature of the particular photoresist and protective coating employed. The most appropriate baking time for any given combination of reactants and bake temperatures can be readily determined by a process of trial and error. The baking step is accomplished using equipment such as a convection oven conventionally employed in the art for this particular operation.

After the baking step, the image and substrate are rinsed using water or appropriate water-miscible solvents, to remove material from areas other than the photoresist image but leaving the photoimage itself coated with a protective layer of the material.

The solutions of thermally stabilizing agents employed to treat the photoresist in the above-described manner can, if desired, contain additives such as surfactants, dyestuffs, stabilizers and the like provided that these additives do not in any way interfere with the desired result of thermally stabilizing the photoresist or affect the subsequent performance of the photoresist. The inclusion of surfactants serves to lower the surface tension of the aqueous solution of film-forming polymeric material and improve the wettability of the surface of the photoresist which is normally hydrophobic.

Surfactants which can be employed, advantageously in a concentration of about 0.05 to about 3 weight per cent, include anionic, cationic and non-ionic surfactants. A preferred group of surfactants are the perfluorocarbons and phosphate esters. As will be obvious to one skilled in the art, no additional surfactant is required when the thermally stabilizing material employed in the process of the invention is a perfluorocarbon surfactant.

Illustrative of the perfluorocarbon surfactants are those which are available from E. I. duPont under the trademark ZONYL and those available from 3M Company under the trademark FLUORAD. Illustrative of phosphate ester surfactants are ethoxylated alcohol phosphate esters available from Jordan Chemical Company.

Any of the dyestuffs known in the art which are compatible with the solution of the thermally stable coating material, and which do not interfere with the thermally stabilizing action of the material or with the subsequent performance of the photoresist, can be employed. Illustrative of such dyestuffs are those of the xanthene type. The presence of the dyestuff in the coating composition and hence in the protective film deposited on the photoresist image greatly facilitates visual inspection of the image.

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The amount of dye, i.e. the concentration in parts by weight, which it is necessary to incorporate into the photoresist in order to facilitate inspection of the coated image after application of the solution containing the dye, will obviously vary depending upon the particular dye in question. In general, it has been found that the minimum amount of dye necessary in any given case is that which will produce an optical density in the solution of film forming polymer of not less than about 10^3 . Optical density (E) is defined by the equation

$$E = \log \frac{I_0}{I}$$

wherein I_0 is the intensity of the incident light and I is the intensity of transmitted (or reflected) light [see for example, Venkataraman, The Chemistry of Synthetic Dyes, Vol. I, p. 310, Academic Press, New York, 1952]. When expressed in terms of proportion by weight in the composition used in the coating, the amount of dye necessary to achieve optical densities of the above order can vary from as little as 0.01 percent by weight to as much as 1 percent by weight or higher depending upon the particular dye under consideration.

The process of the invention serves to impart, to the photoresist image which has been treated, the capability of resisting flow when exposed to temperatures as high as about 220°C. Accordingly, the image so treated is capable of withstanding the temperatures to which it is to be subjected in further processing of the substrate and image supported thereon whether this be by chemical etching or plasma etching and the like, with no unacceptable loss of integrity of the resist image profile. Further, the process of the invention does not interfere with the ease with which the photoresist can be stripped from the substrate when the final step of the overall process is reached. The process of the

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invention is readily carried out in standard equipment, which same equipment is used in other steps of the overall process of forming and end-processing the photoresist image on the substrate.

5 While the process of the invention can be used to thermally stabilize any photoresist image supported on a substrate, it is of particular advantage when utilized in the production and processing of high resolution
10 images required in the production of sub-micron circuitry and the like. The process of the invention will be further illustrated below by reference to its use in treating positive photoresist images but it is to be clearly understood that it is not limited to treatment of such images and can be employed with any photoresist
15 images.

The following examples illustrate the process of the invention and the best mode known to the inventors of carrying out the same but are not to be construed as limiting.

20 Example 1.

A silicon wafer with approximately 10,000 Angstroms of aluminum over 1,000 Angstroms of silicon dioxide was spun-coated at 5000 rpm with a high resolution, high contrast, high aspect ratio positive photoresist system
25 comprising a solvent blend solution of a novolak resin and a trihydroxybenzophenone ester of 2-diazo-1-oxonaphthoquinone-5-sulfonic acid [ULTRAMACtm PR 914; MacDermid Inc., Waterbury, CT]. The coated wafer was baked at 100°C for 30 minutes in a convection oven to
30 evaporate the solvents from the coating before being exposed through a sub-micron geometry mask to UV light in a broad band contact exposure mode using an Oriel printer. The resulting coating had an average thickness of 1.2 microns. The exposed photoresist was developed
35 using an alkaline developer [ULTRAMAC MF-28: MacDermid,

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Inc.] to give an image of high resolution with walls approaching 90 degrees. The imaged wafer was rinsed with water on the vacuum chuck and flooded with an aqueous solution obtained by dissolving 10 g. of gelatin [granular, 100 bloom: Fisher Scientific Company] in sufficient water, at 50°C, to make 1 liter of solution. The wafer was then spun at 2500 rpm for 20 seconds leaving a thin film of gelatin on the photoresist image. The film dried during the spinning operation. The wafer and image was then baked at 160°C for 30 minutes in a convection oven and then rinsed with water at about 50°C. After rinsing and drying, the coated wafer was subjected to a plasma treatment under the following conditions:

15	Plasma Chamber	:	DRYTEK Model 303
	Gas mixture	:	BCl ₃ at 302 SCCM
			Cl ₂ at 8 SCCM
	Pressure	:	124 millitorr
	RF Power	:	1190 watts
20	Temperature at wafer	:	35°C
	Time	:	4 minutes

Inspection of the resulting image using a scanning electron microscope showed no significant distortion or other loss of integrity of the walls of the image.

25 The above procedure was repeated exactly as described except that the step of coating the developed image with gelatin was omitted. It was found that edge rounding of the resulting image was observed when temperatures as low as 120°C were reached in the final baking step. At higher temperatures than 120°C more significant distortion was observed.

Example 2.

35 The procedure of Example 1 was repeated exactly as described except that a post bake temperature of 170°C was employed. Inspection of the photoresist image showed some edge rounding.

Example 3.

The procedure of Example 1 was repeated exactly as described except that a post bake temperature of 180°C was employed. Inspection of the photoresist image after post bake showed significant edge rounding similar to that observed in the absence of a gelatin coating layer. However, after plasma treatment and resist removal, the lines of the final image were found to be straight, sharp and clean with no evidence of distortion.

Example 4.

The procedure of Example 1 was repeated exactly as described except that the novolak resin photoresist system there used was replaced by each of the following commercially available novolak-based systems:

PR64 and EPA914 (MacDermid Inc.)

In all cases the resulting photoresist image showed no significant distortion or other loss of integrity.

Example 5

The procedure of Example 1 was repeated twice exactly as described except that

- (a) in one run the aqueous gelatin solution contained 1 percent w/w of gelatin and 0.2 percent w/w of Rhodamine B;
- (b) in a second run the aqueous gelatin solution contained 2 percent w/w of gelatin and 0.2 percent w/w of Rhodamine B;
- (c) in both runs the baking step was carried out at 170°C for 30 minutes.

Inspection of the resulting image after plasma treatment in each of the two runs showed no significant distortion or other loss of integrity in the walls of the images.

Example 6

The procedure of Example 1 was repeated exactly as described except that 1.5 g. of surfactant [Jordaphos JA-60; Jordan Chemical Company: ethoxylated alcohol phosphate ester] was added to the gelatin solution employed in the coating. After plasma treatment the image was inspected and found to show no significant distortion or other loss of integrity of the walls of the image.

Example 7

The procedure of Example 1 is repeated exactly as described except that 2 g. of Rhodamine B and 1.5 g. of surfactant [Jordaphos JA-60] are added to the gelatin solution employed in the coating.

Example 8

A silicon wafer with approximately 10,000 Angstroms of aluminum over 1,000 Angstroms of silicon dioxide was spun-coated at 5000 rpm with a high resolution, high contrast, high aspect ratio positive photoresist system comprising a solvent blend solution of novolak resin and a trihydroxybenzophenone ester of 2-diazo-1-nxonaphthoquinone-5-sulfonic acid [ULTRAMAC_{tm} PR 914; MacDermid, Inc., Waterbury, CT]. The coated wafer was baked at 100°C for 30 minutes in a convection oven to evaporate the solvents from the coating before being exposed through a sub-micron geometry mask to UV light in a broad band contact exposure mode using an Oriel printer. The resulting coating had an average thickness of 1.2 microns. The exposed photoresist was developed using an alkaline developer [ULTRAMAC MF-28; MacDermid, Inc.] to give an image of high resolution with walls approaching 90 degrees. The imaged wafer was rinsed with water on the vacuum chuck and flooded with an aqueous solution

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obtained by dissolving 10 g. of non-gelling gelatin hydrolysate [hydrolyzed Type B gelatin; molecular weight approximately 2000; protein content above 88%; Peter Cooper Corporations, Oak Creek, Wisconsin; treated to
5 reduce sodium, potassium and iron below 1 ppm] in sufficient water to make 1 liter of solution. The wafer was then spun at 800 rpm for 20 seconds, followed by 4000 rpm for 10 seconds, leaving a thin film of the
10 gelatin hydrolysate on the photoresist image. The film dried during the spinning operation. The wafer and image was then baked at 160°C for 30 minutes in a convection oven and then rinsed with water for 2 minutes in a rinser-drier. After rinsing and drying, the coated wafer was subjected to a plasma treatment under the
15 following conditions:

Plasma Chamber	:	DRYTEK Model 303
Gas mixture	:	BCl ₃ at 302 SCCM Cl ₂ at 8 SCCM
Pressure	:	124 millitorr
20 RF Power	:	1190 watts
Temperature at wafer	:	35°C
Time	:	4 minutes

Inspection of the resulting image using a scanning electron microscope showed no significant distortion or
25 other loss of integrity of the walls of the image.

Example 9

A silicon wafer with an oxide coating was spun-coated at 5000 rpm with a high resolution, high contrast, high aspect ratio positive photoresist system
30 comprising a solvent blend solution of a novolak resin and a trihydroxybenzophenone ester of 2-diazo-1-oxo-naphthoquinone-5-sulfonic acid [ULTRAMAC[™] PR 914; MacDermid, Inc., Waterbury, CT]. The resulting coating had an average thickness of 1.2 microns. The coated
35 wafer was baked at 100°C for 30 minutes in a convection

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oven to evaporate the solvents from the coating before being exposed through a submicron geometry mask to UV light in a broad band contact exposure mode using an Oriel printer. The exposed photoresist was developed using an alkaline developer [ULTRAMAC MF-28: MacDermid, Inc.] to give an image of high resolution with walls approaching 90 degrees. The wafer with image attached was rinsed with water, mounted in a vacuum chuck and flooded with an aqueous solution obtained by diluting 3 parts by weight of FLUORAD FC-99 [believed to be a 25% w/w aqueous solution of an amine salt of perfluoroalkyl-sulfonic acid; 3M Company] with 1 part by weight of water. The wafer was then spun at 6000 rpm for 20 seconds leaving a thin film of the perfluoroalkylsulfonate surfactant on the photoresist image. The film dried during the spinning operation. The wafer and image was then baked at 160°C for 30 minutes in a convection oven and then rinsed with water. Inspection of the resulting image using a scanning electron microscope showed no significant distortion or other loss of integrity of the walls of the image.

The above procedure was repeated exactly as described except that the step of coating the developed image with the perfluoroalkylsulfonate surfactant was omitted. It was found that edge rounding of the resulting image was observed when temperatures as low as 120°C were reached in the final baking step. At higher temperatures than 120°C more significant distortion was observed.

Example 10

A series of positive photoresist high resolution images on silicon wafers was prepared using the procedure described in Example 1 but varying the concentration of perfluoroalkylsulfonate surfactant (FLUORAD FC-99 used in all runs), the nature of the

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photor sist, the spin time (20 seconds in all cases) in spin coating of the image, and the temperature of baking. The various parameters are summarized in TABLE 1 below. The images produced in all the runs were inspected using a scanning electron microscope and were found to have suffered no significant distortion or other loss of integrity of the walls of the image during the exposure to the baking temperature. In the case of Run 2K the photoresist, after the baking step, was stripped without difficulty using a proprietary resist stripper (S41; MacDermid, Inc.) at 100°C in 2.5 minutes.

TABLE 1

	<u>Run No.</u>	<u>Concⁿ of FC-99 (% solids)</u>	<u>Photoresist</u>	<u>Spin RPM</u>	<u>Bake Temp °C</u>
15	2A	12.5	PR 914	1000	150
	2B	12.5	"	2500	150
	2C	18.75	"	6000	160
	2D	25	"	1000	150
20	2E	25	"	5000	150
	2F	25	"	6000	150
	2G	18.75	AZ 4110 ¹	6000	150
	2H	18.75	HPR 204 ²	6000	150
	2I	18.75	PR 643	6000	150
25	2J	18.75	EPA 914 ⁴	6000	150
	2K	12.5	PR 914	6000	175

Footnotes to TABLE 1

1. Novolak resin based positive resist : Shipley Company, Inc.

30 2. Novolak resin based positive resist : Hunt Chemical

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3. Novolak resin based positive resist : MacDermid, Inc.
4. Novolak resin based positive resist : MacDermid, Inc. Run No. 2K was repeated without carrying out the coating with FC-99. Post baking at 175°C caused marked flow of the image and rendered the latter difficult to strip from the substrate.

Example 11

The process of Example 1 was repeated exactly as described except that the fluorocarbon surfactant there used was replaced by a 0.5% w/w aqueous solution of FLUORAD FC 98 (potassium perfluoroalkylsulfonate; 3M Company) and the spin coating of the image with this surfactant was carried out for 20 second at 6000 rpm. The resulting image was found to have undergone no edge rounding or flow during the baking process (150°C for 30 minutes).

Example 12

The process of Example 3 was repeated but replacing the FLUORAD FC98 solution by a 0.1% w/w aqueous solution of FLUORAD FC95 (potassium perfluoroalkylsulfonates : 3M Company). Again it was found that the so treated image suffered no edge rounding or flow during the baking process at 150°C for 30 minutes.

Example 13

The process of Example 3 was repeated but replacing the FLUORAD FC98 solution by a 25% by weight solids solution of FLUORAD FC93 (ammonium perfluoroalkylsulfonates; 3M Company) in an isopropyl alcohol-water solution (27% by weight isopropyl alcohol). Again it was found that the so treated image suffered no edge rounding or flow during the baking process at 150°C for 30 minutes.

Example 14

The process of Example 1 was repeated except that the FC surfactant was replaced by a solution of ZONYL FSA ("Dupont"), believed to be the lithium salt of a mixed fluorocarbon-hydrocarbon carboxylic acid (50% (wt) in a mixture of water and isopropyl alcohol), spin-coated at 5000 rpm. After a post bake of 150°C for 30 minutes, there was no image flow (but line edges were somewhat irregular).

Example 15

The process of Example 1 was repeated except that the FC surfactant was replaced by a solution of polyvinyl alcohol (5% by wt. in water), spin-coated at 5000 rpm. After a post bake at 140°C for 30 minutes a slight edge rounding was seen whereas in Example 1 (second portion, without FC), edge-rounding was noted at 120°C.

Example 16

The process of Example 1 was repeated except that the FC surfactant was replaced by a solution of 10% by wt. chromium trioxide in water, spin-coated at 1000 rpm for 20 seconds. After a post bake at 140°C for 30 minutes, some partial edge-rounding was visible.

Example 17

The process of Example 1 was repeated except that the FC surfactant was replaced by a solution of chromotropic acid, (disodium salt), 10% wt. in water, spin-coated at 1000 rpm for 20 seconds. After a 140°C post bake for 30 minutes, some partial edge-rounding was noted.

Example 18

Plasma Treatment (SiO₂)

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The process of Example 1 was repeated and after treatment with the thermal stabilizing solution, the wafer was post baked at 140°C for 30 minutes and exposed to plasma treatment under the following conditions:

5	Plasma Chamber	DRYTEK Model 202
	Gas Mixture	C ₂ F ₆ at 150 SCCM, CHF ₃ at 3 SCCM and CO at 104 SCCM
	Pressure	751 millitorr
10	RF Power	1500 Watts
	Temperature at Wafer	25°C
	Time	4 minutes

The resist thickness loss was 11%, with clean and sharp edge definition. There was no surface pitting on the resist nor any changes in the critical dimensions.

A control wafer without the thermal stabilizing treatment showed significant edge rounding after the post bake and before plasma treatment. After plasma, the pattern was transferred through the oxide leaving somewhat rounded edges and changes in the critical dimensions.

Example 19

Plasma Treatment (Al)

The process of Example 1 was repeated on a wafer of aluminum alloy (96% Al, 4% Cu). After treatment with the thermal stabilizing solution, the wafer was post baked at 125°C for 30 minutes and subjected to plasma treatment.

	Plasma Chamber	DRYTEK Model 203
30	Gas Mixture	BCl ₃ at 302 SCCM, Cl ₂ at 18 SCCM
	Pressure	124 millitorr
	RF Power	1300 Watts
	Temperature at Wafer	35°C
35	Time	4 minutes, followed by

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anti-corrosion treatment of
30 second in SF_6 at 100
SCCM, 125 millitorr and 450
Watts, RF.

5 The etched surface showed straight edges with no
rounding or apparent critical dimension change. The
resist thickness loss was 20%.

10 A control wafer without the thermal stabilizer
treatment showed a 40% loss in resist thickness. There
was edge rounding after the post bake which was trans-
ferred to the image.

15 The difference in the resist thickness losses over
the aluminum substrate versus the silicon dioxide (see
Example 10) is caused by the difference in plasma gases
used.

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WHAT IS CLAIMED IS:

1. A process for thermally stabilizing a photoresist image layer formed on a substrate, said process comprising coating said image layer with a protective film of a thermally stabilizing material prior to subjecting said image layer to a post-development bake.
5
2. A process according to claim 1 wherein said thermally stabilizing material is selected from film-forming polymers, chromium sulfate, trichloroacetic acid, chromotropic acid and salts thereof, and fluorocarbon surfactants.
5
3. A process according to claim 1 wherein said thermally stabilizing material is a perfluorocarbon surfactant.
4. A process according to claim 3 wherein said perfluorocarbon surfactant is selected from the class consisting of perfluorocarbon carboxylic acids, perfluorocarbon-sulfonic acids, perfluorocarbon phosphonic acids, and alkali metal, ammonium and amine salts of said acids, ethoxylated perfluorocarbon alcohols, and quaternary ammonium salts of N-perfluoroalkyl-N', N"-dialkylamines.
5
5. A process according to claim 3 wherein said perfluorocarbon surfactant is a perfluorocarbon sulfonic acid in the form of the free acid or a salt thereof.
6. A process according to claim 1 wherein said thermally stabilizing material comprises a hydrolyzed collagen.

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7. A process according to claim 6 wherein said hydrolyzed collagen comprises gelatin.
8. A process according to claim 6 wherein said hydrolyzed collagen comprises a non-gelling gelatin hydrolysate.
9. A process according to claim 1 wherein said post-development bake is carried out at a temperature within the range of about 100°C to about 190°C.
10. A process according to claim 1 wherein the thermally stabilizing material is applied as a solution to the photoresist image layer by spin coating.
11. A process according to claim 10 wherein the thermally stabilizing material is present in said solution in an amount within the range of about 0.1 to about 25 percent by weight.
12. A process according to claim 1 wherein said image layer has been produced using a positive photoresist resin.
13. A process according to claim 12 wherein said positive photoresist resin comprises a novolak resin and a sensitizer and said image layer has been developed using an alkaline developer.
14. A process for forming a heat stabilized positive photoresist image layer which comprises the steps of coating a substrate with a layer of a positive photoresist composition, irradiating said layer through a mask, developing the image layer so produced, coating said developed image layer with a film of a thermally

stabilizing material and subjecting the coated layer to a post-development bake at a temperature within the range of about 110°C to about 170°C.

15. A process according to claim 14 wherein said film of thermally stabilizing material also comprises a surfactant.

16. A process according to claim 14 wherein said film of thermally stabilizing material also comprises a dyestuff compatible therewith.

5 17. A process for thermally stabilizing a photoresist image layer formed on a substrate, said process comprising coating said image with a solution of non-gelling gelatin hydrolysate prior to subjecting said image layer to a post-development bake.

18. A process according to claim 17 wherein said gelatin hydrolysate solution also comprises a surfactant.

19. A process according to claim 18 wherein said surfactant is a phosphate ester.

20. A process according to claim 17 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin.

21. A process according to claim 18 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin.

22. A process according to claim 19 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin hydrolysate.

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23. A process according to claim 17 wherein the gelatin hydrolysate is applied to said image layer as an aqueous solution containing from about 0.1 to about 10 percent by weight of gelatin hydrolysate.

24. A process according to claim 17 wherein said photoresist image is derived from a positive photoresist composition comprising a solvent solution comprising a novolak resin and a photosensitizer.

25. A process according to claim 24 wherein the image layer has been developed using an alkaline developer.

26. A process according to claim 17 wherein said thermally stabilizing material is spin-coated on said image layer in the form of an aqueous solution.

27. A process according to claim 17 wherein said post-development bake is carried out at a temperature within the range of about 100°C to about 180°C.

28. A coating composition for thermally stabilizing a photoresist image layer formed on a substrate said composition comprising an aqueous solution comprising from about 0.1 to 10 weight percent of gelatin hydrolysate and from about 0.05 to 3.0 weight percent of a surfactant.

29. A composition according to claim 28 wherein said surfactant is a phosphate ester.

30. A composition according to claim 28 which also comprises a dyestuff compatible with said gelatin hydrolysate, said dyestuff being present in an amount sufficient to produce an optical density in said composition of not less than about 10^{-3} .

5 31. A coating composition for thermally stabilizing a photoresist image layer formed on a substrate said composition comprising an aqueous solution comprising gelatin hydrolysate and a dyestuff compatible with said gelatin hydrolysate, said dyestuff being present in an amount sufficient to produce an optical density in said composition of not less than about 10^3 .

32. A photoresist image which has been thermally stabilized in accordance with the process of claim 1.

33. A photoresist image which has been thermally stabilized in accordance with the process of claim 17.

AMENDED CLAIMS

[received by the International Bureau on 30 March 1987 (30.03.87);
original claims 1-33 replaced by amended claims 1-32 (4 pages)]

1. A process for thermally stabilizing a photoresist layer formed on a substrate, said process comprising coating said image layer with a protective film of a thermally stabilizing material selected from fluorocarbon surfactants, chromotropic acid and salts thereof and hydrolyzed collagens prior to subjecting said image layer to a post-development bake.
2. A process according to claim 1 wherein said thermally stabilizing material is a perfluorocarbon surfactant.
3. A process according to claim 2 wherein said perfluorocarbon surfactant is selected from the class consisting of perfluorocarbon carboxylic acids, perfluorocarbon-sulfonic acids, perfluorocarbon phosphonic acids, and alkali metal, ammonium and amine salts of said acids, ethoxylated perfluorocarbon alcohols, and quaternary ammonium salts of N-perfluoroalkyl-N', N''-dialkylamines.
4. A process according to claim 2 wherein said perfluorocarbon surfactant is a perfluorocarbon sulfonic acid in the form of the free acid or a salt thereof.
5. A process according to claim 1 wherein said thermally stabilizing material comprises a hydrolyzed collagen.
6. A process according to claim 5 wherein said hydrolyzed collagen comprises gelatin.
7. A process according to claim 6 wherein said hydrolyzed collagen comprises a non-gelling gelatin hydrolysate.
8. A process according to claim 1 wherein said post-development bake is carried out at a temperature within the range of about 100°C to about 190°C.

9. A process according to claim 1 wherein the thermally stabilizing material is applied as a solution to the photoresist image layer by spin coating.

10. A process according to claim 9 wherein the thermally stabilizing material is present in said solution in an amount within the range of about 0.1 to about 25 percent by weight.

11. A process according to claim 1 wherein said image layer has been produced using a positive photoresist resin.

12. A process according to claim 11 wherein said positive photoresist resin comprises a novolak resin and a sensitizer and said image layer has been developed using an alkaline developer.

13. A process for forming a heat stabilized positive photoresist image layer which comprises the steps of coating a substrate with a layer of a positive photoresist composition, irradiating said layer through a mask, developing the image layer so produced, coating said developed image layer with a film of a thermally stabilizing material selected from fluorocarbon surfactants, chromotropic acid and salts thereof and hydrolyzed collagens, and subjecting the coated layer to a post development bake at a temperature within the range of about 110°C to about 170°C.

14. A process according to claim 13 wherein said film of thermally stabilizing material also comprises a surfactant.

15. A process according to claim 13 wherein said film of thermally stabilizing material also comprises a dye-stuff compatible therewith.

16. A process for thermally stabilizing a photoresist image layer formed on a substrate, said process comprising coating said image with a solution of non-gelling gelatin hydrolysate prior to subjecting said image layer to a post-development bake.

17. A process according to claim 16 wherein said gelatin hydrolysate solution also comprises a surfactant.

18. A process according to claim 17 wherein said surfactant is a phosphate ester.

19. A process according to claim 16 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin.

20. A process according to claim 17 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin.

21. A process according to claim 18 wherein said gelatin hydrolysate solution also comprises a dyestuff compatible with said gelatin hydrolysate.

22. A process according to claim 16 wherein the gelatin hydrolysate is applied to said image layer as an aqueous solution containing from about 0.1 to about 10 percent by weight of gelatin hydrolysate.

23. A process according to claim 16 wherein said photoresist image is derived from a positive photoresist composition comprising a solvent solution comprising a novolak resin and a photosensitizer.

24. A process according to claim 23 wherein the image layer has been developed using an alkaline developer.

25. A process according to claim 16 wherein said thermally stabilizing material is spin-coated on said image layer in the form of an aqueous solution.

26. A process according to claim 16 wherein said post-development bake is carried out at a temperature within the range of about 100°C to about 180°C.

27. A coating composition for thermally stabilizing a photoresist image layer formed on a substrate said composition comprising an aqueous solution comprising from about 0.1 to 10 weight percent of gelatin hydrolysate and from about 0.05 to 3.0 weight percent of a surfactant.

28. A composition according to claim 27 wherein said surfactant is a phosphate ester.

29. A composition according to claim 27 which also comprises a dyestuff compatible with said gelatin hydrolysate, said dyestuff being present in an amount sufficient to produce an optical density in said composition of not less than about 10^3 .

30. A coating composition for thermally stabilizing photoresist image layer formed on a substrate said composition comprising an aqueous solution comprising gelatin hydrolysate and a dyestuff compatible with said gelatin hydrolysate, said dyestuff being present in an amount sufficient to produce an optical density in said composition of not less than about 10^3 .

31. A photoresist image which has been thermally stabilized in accordance with the process of claim 1.

32. A photoresist image which has been thermally stabilized in accordance with the process of claim 16.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02441

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT CL 4 G03C 5/00		
US CL 430/325, 326, 330, 331; 106/135, 137		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
U.S.	430/322, 325, 326, 328, 330, 331 106/135, 137	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,652,274 (VERELST) 28 MARCH 1972. See the entire document.	1, 12, 32
X Y	US, A, 4,125,650 (CHIU) 14 NOVEMBER 1978. See the entire document.	1-3, 9-15, 32. 4, 5, 16
Y	IBM Technical Disclosure Bulletin, volume 21, No. 8, January 1979 (Armonk, New York), KAPLAN, "Photoresist hardening Techniques for Profile Stability, page 3205.	3, 4
P, Y	US, A, 4,565,771 (LYNCH) 21 JANUARY 1986. See the entire document.	2
Y	IBM Technical Disclosure Bulletin, volume 20, No. 8, January 1978, (Armonk, New York), ECONOMY, "Enhanced Thermal Stability of Resist. . .," page 3259.	1
Y	IBM Technical Disclosure Bulletin, Vol. 20, No. 7, December 1977 (Armonk, New York), CHIU, "Oxidation Hardening Technique for Developed Resist Films", page 2706.	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁶</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
22 DECEMBER 1986	05 FEB 1987	
International Searching Authority *	Signature of Authorized Officer ¹⁹	
ISA/US	JOSE DEES	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-27, 32 and 33 drawn to a process for thermally stabilizing a photoresist image; class 430, subclass 322.

II. Claims 28-31 drawn to a coating composition; class 106, subclass 135

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone practice

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

III. D CUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
X	US,A, 4,187,331 (HSIOH-LEIN MA) 05 FEBRUARY 1980. See the entire document.	1
A	US,A, 4,259,369 (CANAVELLO) 31 MARCH 1981. See the entire document.	1
X	US,A, 3,881,929 (ASAKAWA) 06 MAY 1975. See claims 1-3.	28
Y	US,A, 3,859,098 (IWAMA) 07 JANUARY 1975. See column 9, lines 37-67 and column 10, lines 4-12.	1, 2, 10, 11, 16

ATTACHMENT TO FORM PCT/ISA/210, Part VI, 1.

Telephone approval:

\$140 payment approved by Mr. Stonge on 18 DECEMBER 1986 for Group II; charge to Deposit Account No. 19-4516. Counsel advised that he has no right to protest for any group not paid for and that any protest must be filed no later than 15 days from the date of mailing of the search report (Form 210).

Reasons for holding lack of unity of invention:

The invention as defined by Group I (claims 1-27, 32 and 33) is drawn to a process for thermally stabilizing a photoresist image which is classified in class 430, subclass 322 and which can be practiced by another and materially different product than that invention of Group II (claims 28-31) which is drawn to a coating composition and is classified in class 106, subclass 135, i.e., using an aqueous gelatin solution without a surfactant or dyestuff in the process of thermally stabilizing a photoresist image.

Time Limit for Filing A Protest

Applicant is hereby given 15 days from the mailing date of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2 applicant may protest the holding of lack of unity only with respect to the group(s) paid for.

